Specific Heats and Heats of Dilution of Concentrated Sodium Hydroxide Solutions

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A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF SCIENCE
IN THE UNIVERSITY OF MICHIGAN

By
Howard R. Wilson
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Specific Heats and Heats of Dilution of Concentrated Sodium Hydroxide Solutions

Howard R. Wilson[1] *and Warren L. McCabe*[2]

University of Michigan, Ann Arbor, Mich.

Data are presented on the specific heats of caustic soda solutions over a concentration range of 50.2 to 75.9 weight per cent and a temperature range of 81.6° to 254.6° F., and on heats of dilution over a concentration range of 48.64 to 75.51 weight fraction at 200° F. The results have been combined with existing data for lower concentrations, and an enthalpy-concentration chart has been constructed covering a range of 0 to 80 weight per cent of sodium hydroxide and a temperature range 100° to 400° F. The enthalpies at the higher temperatures (250° to 400° F.) were obtained by extrapolating specific heat data, but these enthalpies should be adequate for engineering calculations.

THE thermal properties of common commercial solutions in concentrated form are important in engineering. The purpose of this paper is to present new data on the enthalpies of concentrated sodium hydroxide solutions. Previous papers (*1*, *2*) gave data for specific heats of sodium hydroxide solutions over a concentration range of 4 to 51 weight per cent and a temperature range of 37° to 191° F., and for heats of dilution over a range of 0 to 48 weight per cent at 68° F. The present work extends these data to 78 weight per cent sodium hydroxide.

The principles and technique of adiabatic calorimetry for determining the thermal properties of solutions are well known (*4–8*). The essential feature of the method is the principle used to eliminate the radiation correction. Heat transmission between the reaction bomb and its surroundings is minimized by interposing an air gap between the bomb and the jacket, and immersing the jacket in a liquid bath maintained at a temperature equal to that of the bomb and its contents. To ensure reasonable uniformity of temperature, the liquid in the bomb is stirred at a constant rate. The stirring causes a slow, constant upward drift of bomb temperature. To maintain adiabatic conditions, a corresponding upward drift of bath temperature is created by the addition of heat to the bath.

After the heat effect of the reaction in the bomb has been absorbed (either heat added electrically in a specific heat determination or the heat released by mixing in a heat of dilution determination), the bomb temperature resumes its upward drift, again because of the energy of stirring. The rate of the afterdrift is nearly equal to that of the foredrift.

[1] Present address, National Carbon Company, Cleveland, Ohio.
[2] Present address, Carnegie Institute of Technology, Pittsburgh, Penna.

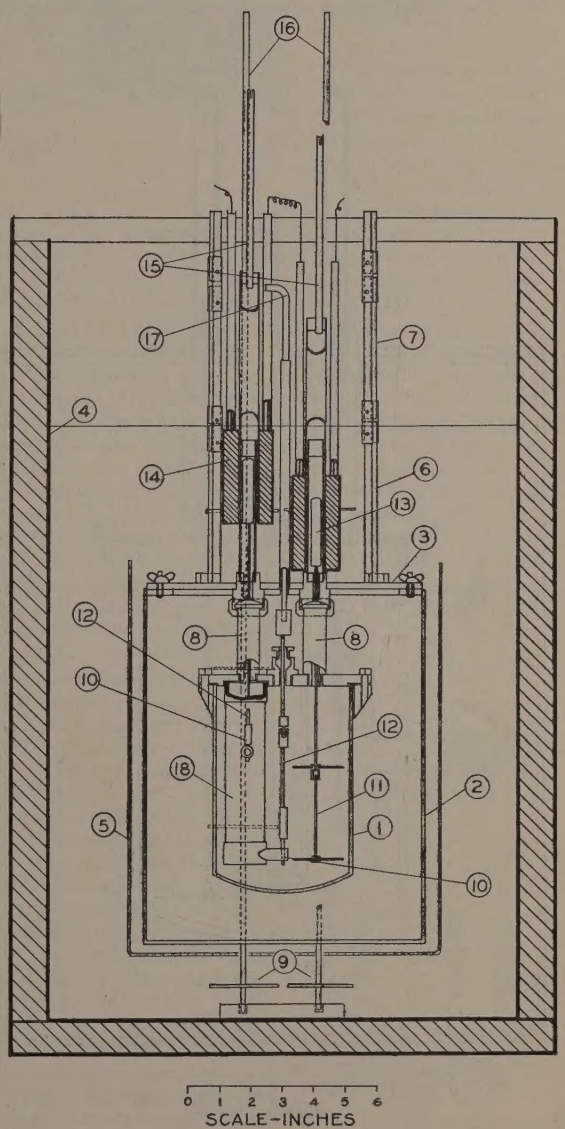

Figure 1. General View of Calorimeter

and the net temperature rise for the experiment is found by extrapolating the time-temperature drift plots to the mid-time of the experiment and reading the temperature difference between two straight lines at that time, as shown by Bertetti and McCabe (*2*). In the present investigation all temperatures were measured potentiometrically. Multijunction thermocouples were used as primary temperature elements.

A small correction is made for the heat effect accompanying the vaporization of water from the solution into the vapor space above the solution. On the assumptions that the vapor space contains a definite and constant mass of air, that the air is in equilibrium with the solution at both initial and final conditions and that the perfect gas laws apply, the evaporation is:

$$w = \frac{V}{R}\left(\frac{p_2}{T_2} - \frac{p_1}{T_1}\right) \quad (1)$$

where w = moles of water vaporized
V = volume of vapor space
R = gas constant
p_1 = partial pressure of water vapor at start of experiment
p_2 = partial pressure of water vapor at end of experiment
T_1 = absolute temperature at start of experiment
T_2 = absolute temperature at end of experiment

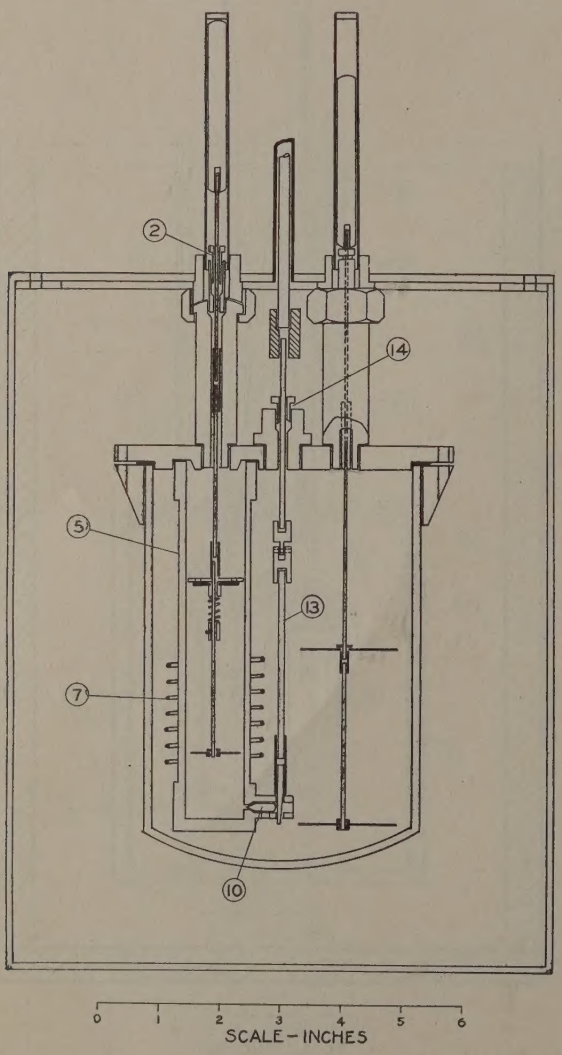

Figure 2. Details of Bomb

Apparatus

The apparatus used in this investigation incorporated features suggested by White (*8*) and consisted essentially of an adiabatic working calorimeter, a cascade cold calorimeter, and an ice bath. The general arrangement was described by Bertetti and McCabe (*2*); the cold calorimeter or intermediate reference calorimeter and ice bath were substantially the same as they used. The working calorimeter is shown in Figures 1, 2, and 3. Figures 1 and 2 show the calorimeter fitted with a dilution cup (Figure 4) which is used in the measurement of heats of dilution. In the determination of specific heats a quantitative heating coil replaced the dilution cup (Figure 3). All parts in contact with the sodium hydroxide solution were either made of pure nickel or were heavily plated.

The bomb, 1 (Figure 1), was made by welding a dished nickel bottom to a section of 4.5-inch o. d., 11-gage nickel tubing 6 inches long. The top was threaded and fitted with a flange that registered with a 3/8-inch thick, nickel-plated steel cover. An asbestos-rubber composition gasket was used. The cover of the bomb was suspended by porcelain insulating posts within the submarine jacket, 2. The submarine was fitted with a watertight cover, 3, and was completely immersed in a liquid bath held in copper container 4. An insulating air gap therefore existed between the bomb and the surrounding bath. Water was used in the bath for runs at temperatures below 70–80° C. (158–176° F.), and 95 per cent glycerol for runs at higher temperatures.

The submarine assembly containing the bomb was suspended from a permanent frame by steel bars, 6, insulated by Bakelite strips, 7. The submarine was surrounded by the expanded metal screen, 5, which served as one electrode for the electrolytic heating of the bath. The inside wall of copper container 4 served as the grounded return. Alternating 110-volt current supplied the heat to the bath. The expanded metal screen was used as an electrode instead of the submarine to prevent overheating of the submarine above the temperature of the surrounding bath. The surrounding bath was vigorously stirred by propeller-type stirrers, 9, on vertical shafts, 16, operating at approximately 1500 r. p. m. The agitation from the stirrers and the uniform liberation of heat throughout the solution characteristic of electrolytic heating gave uniform temperature distribution. The current was controlled by water-cooled rheostats. The difference in temperature between bomb contents and bath was indicated by a sensitive galvanometer connected over a twelve-junction thermoelement; one set of these junctions was enclosed in a nickel sheath immersed in the solution in the bomb, and the other junctions were enclosed in a copper sheath immersed in the bath surrounding the submarine jacket. The temperature of the bath could be rapidly adjusted by varying the input of current, and the temperature of the bomb could easily be duplicated by the temperature of the bath to within about 0.05° C. (0.09° F.).

To reduce thermal lags within the bomb, the solutions were thoroughly stirred by two reciprocating dasher-type stirrers, one of which, 11, is shown in Figure 1. The other is enclosed in the dilution cup as shown in Figure 2. The stirrers were moved by the constant reciprocating action of connecting rods 15, attached to magnetic solenoids, 14, surrounding the armatures, 13. The armatures moved inside closed brass tubes which were mounted above the porcelain bomb support bushings, 8, through which passed 1/16-inch-diameter nickel stirring rods connecting the armatures with the nickel agitators in the bomb below. The entire stirring system for the bomb was thus completely sealed. This arrangement eliminated

the possibility of loss of water vapor which might escape if packing glands had to be used to bring the stirring rods out of the bomb.

The bomb is shown in Figures 2 and 3. Stuffing boxes 2 (Figure 2) were used inside the armature chambers as an added precaution to minimize vapor diffusion into these chambers from the vapor space in the bomb. This loss was not important in view of the fact that the heat radiated from the solenoids maintained a temperature in the armature chambers enough higher than that in the bomb to prevent condensation. To minimize heat conduction along stirring rods and valve control rods, Bakelite and glass couplings were placed between sections of these rods where they passed through the cover of the bomb.

In determining heats of dilution the dilution cup shown at 18 in Figure 1 and at 5 in Figure 2 was used. The cup held about 70 cc. of liquid. The valves, 10, were controlled by rods 12 and 17 (Figure 1). In Figure 3 the bomb is suspended below the cover to show the arrangement of parts inside the calorimeter when the calorimeter is fitted with the quantitative heating coil used in specific heat determination.

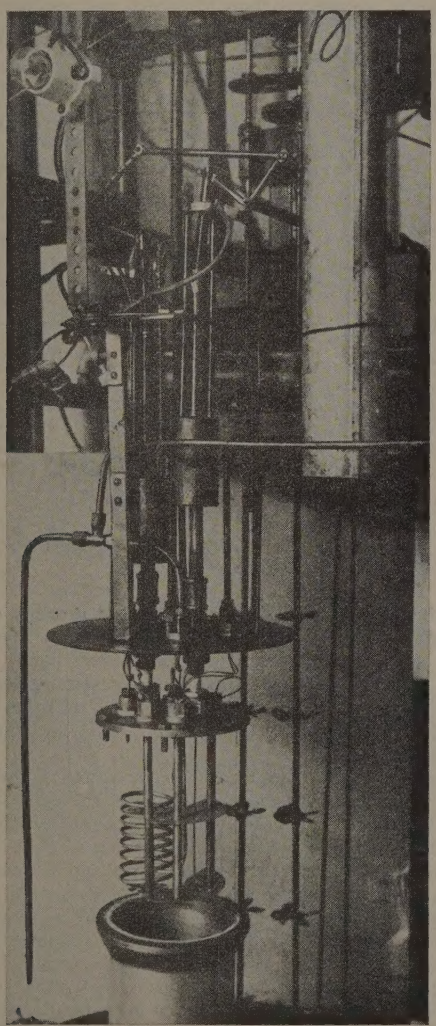

Figure 3. Bomb, Stirring Assembly, and Heating Coil

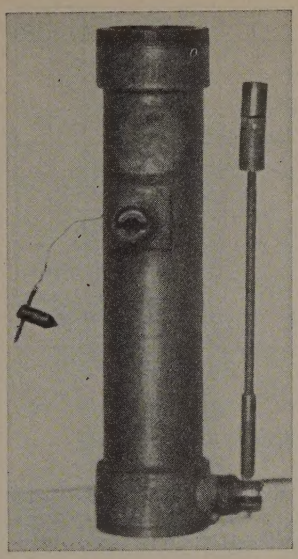

Figure 4. Dilution Cup and Valve

The electrical insulation of the thermocouples, heating elements, and lead wires was selected so that a temperature of 170° C. could be attainable before significant electrical leakages would develop. Wires used for thermoelements were No. 30 enameled constantan and No. 40 enameled and silk-covered copper. Junctions were smooth beads formed by electric welding, and the exposed surface was insulated by several coats of General Electric Insulating Compound No. 1202 baked at 180–200° C. (356–392° F.). The insulating properties of the compound were improved by incorporating 20 per cent by weight of powdered mica. Clear varnish was applied throughout the length of the thermoelements to prevent electrical leakage to the metal sheaths.

A calibrated twelve-junction thermoelement was used to read the difference in temperature between the bomb of the working calorimeter and a copper block inside the reference calorimeter. A two-junction element (originally four-junction) measured the difference in temperature of the reference calorimeter and an ice bath. The thermoelements were calibrated in a well-stirred oil bath by comparison with the temperatures indicated by a platinum resistance thermometer immersed in the bath and positioned close to the thermocouple. The thermocouple system was essentially the same as that used by Bertetti and McCabe (*2*). Calibration of the resistance thermometer was checked at the ice point, at the transition point of pure $Na_2SO_4.10H_2O$, and at the melting point of pure tin, and empirical equations were fitted to the data so that temperatures could be calculated accurately from the e. m. f. readings.

The quantitative heating coil, 7 (Figure 2), consisted of a constantan heating wire enclosed in a nickel-plated brass tube with glass tubing around the wire and inside the brass tube. In making the coil, the wire and glass tubing were slid inside the straight brass tube, and the whole assembly was rolled into a coil while being heated to red heat in a gas flame. The glass insulation was better for high-temperature work than asbestos-covered wire since electrical leakage was eliminated.

The dilution cup, 5 (Figure 2), contained two valves, 10,

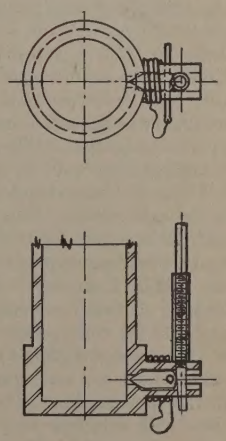

Figure 5. Valve of Dilution Cup

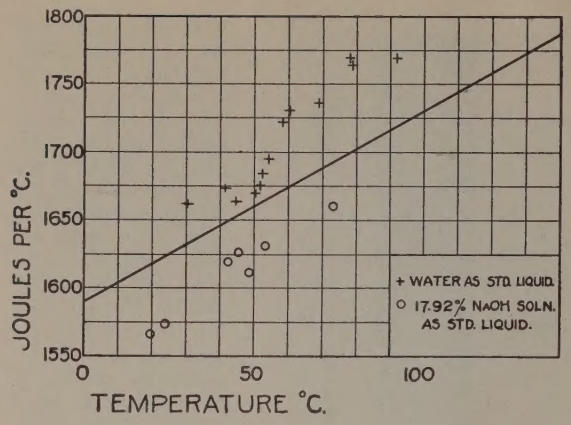

Figure 6. Thermal Capacity of Calorimeter

operated by valve rods, 13, that emerged from the bomb through stuffing boxes, 14. One valve was placed at the bottom of the cup as shown in Figure 2. The second valve was placed about one third of the distance and 90° from the first valve around the circumference as shown in Figure 1 at 10. The details of a valve are shown in Figure 5. Each valve is closed by wedging the valve plug against the valve seat with a tapered stem. The valve seat was slotted to take a small nickel rod that passed through the plug, and a nickel-plated steel spring acted on the rod against the thrust of the wedge. The wedge could be loosened and the valve "cracked" by turning the valve rod which caused the wedge to rise through the action of the screw threads of the coupling and gradually free the plug. A step was cut on the wedge to provide a definite cracked position to reduce the violence of the reaction during the first portion of a dilution. By lifting the valve rod, the valve could be opened completely as the spring snapped the plug clear of the valve.

Solutions

The sodium hydroxide solutions were stored in nickel beakers, in a nickel evaporator under an atmosphere of nitrogen, or in thermoprene-lined glass vessels. The latter were used only for solutions below 55 per cent concentration which were liquid at room temperature. There were two sources of sodium hydroxide. The first was C. P. stick sodium hydroxide. Solutions were prepared by crystallizing sodium hydroxide monohydrate from solution and dissolving the monohydrate to form a saturated solution at room temperature. Under these conditions the solubility of sodium carbonate is very low, and it is readily separated by settling. The clear solution was decanted and evaporated to 75 per cent sodium hydroxide content. The concentrated solution was blown to the calorimeter bomb by nitrogen pressure. A glass plate was laid over the bomb until it was raised into position for sealing in the calorimeter. The second source of sodium hydroxide, and the one used for the greater part of the work on specific heats, was Mercury-Cell liquid caustic supplied by the Mathieson Alkali Company. The analysis of the material was 69.4 per cent sodium hydroxide, 0.14 per cent sodium chloride, and 0.14 per cent sodium carbonate. This was concentrated to 75.9 per cent sodium hydroxide content in the nickel evaporator under an atmosphere of nitrogen and used without further purification. The results of specific heat determinations with solutions from each source agreed within the experimental error of the determination.

The total sodium content of the solutions was determined analytically by weighing the sodium chloride formed when the sample was treated with a slight excess of hydrochloric acid, evaporated to dryness at 115–125° C. (239–257° F.), and heated for 2 hours at 350° C. (662° F.). The method is that of Richards and Hall (*5*).

Heat Capacity of Calorimeter

The heat capacity of the calorimeter was found by three methods. In the first and second methods it was determined experimentally by adding a measured quantity of heat electrically by the quantitative heating coil. The calorimeter was charged with a standard liquid, the specific heat of which was known. The temperature accompanying the addition of the electrical energy was determined. The heat absorbed by the liquid was calculated from its known specific heat and the weight of the liquid, and was subtracted from the total heat added. The difference divided by the temperature rise gave the thermal capacity of the calorimeter. The correction for vaporization was applied. Of the total heat added, approximately one fourth was absorbed by the calorimeter and three fourths by the liquid.

In the first experimental method water was used as the standard liquid, and in the second a solution containing 17.92 weight per cent sodium hydroxide was chosen. The specific heat of this solution was known from the results of Bertetti and McCabe (*2*).

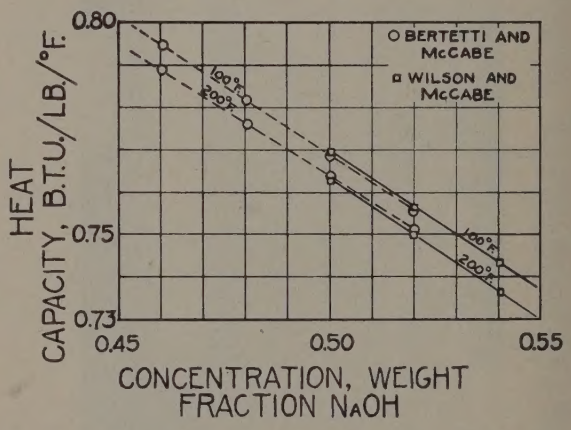

Figure 7. Comparison of Specific Heats with Data of Bertetti and McCabe

The third method of determining the heat capacity of the calorimeter was to calculate the heat capacity from the weights and specific heats of the calorimeter parts. This method is less certain than experimental determinations because of the uncertainty of specific heats. On the other hand, the calculation is suitable to find the slope of the heat capacity –temperature relation.

The experimental values for the heat capacity of the calorimeter determined with water as the standard liquid differed by 3 to 4 per cent from those found when the sodium hydroxide solution was used. A mean line having a slope determined by the calculations made in method 3 and intermediate between the results of the two types of experimental determination was chosen as the final value for the heat capacity of the calorimeter. This line and the experimental points are shown in Figure 6. If values from the straight line of Figure 6 are accepted for the heat capacity of the calorimeter, the specific heats determined in the present investigation for solutions of about 50 weight per cent sodium hydroxide agree well with those found by Bertetti and McCabe for the same concentration range. The comparison is shown in Figure 7.

TABLE I. RESULTS OF SPECIFIC HEAT DETERMINATIONS

Run No.	Wt. in Grams; Concn. of Soln., %	Av. Temp., ° C.	Temp. Rise Δt, ° C.	Total Heat Input, Joules	Cor. for Evapn., Joules	Heat to Bomb, Joules	Heat to Soln., Joules	(Δt) × Wt. of Soln.	Specific Heat: Joules/gram/° C.	Specific Heat: B. t. u./lb./° F.
1	2036; 51.5	31.35	1.3865	11,297.6	0.03	2,253.1	9,044.5	2,822.9	3.204	0.7651
2	2254; 71.1	74.11	1.7112	13,332.8	0.11	2,874.8	10,457.9	3,857.0	2.7114	0.6475
3		75.865	1.7053	13,273.0	0.11	2,870.0	10,402.9	3,843.7	2.7065	0.6463
4		80.35	2.0978	16,414.3	0.21	3,543.2	12,870.9	4,728.4	2.7220	0.6500
5		82.30	1.6795	13,079.3	0.16	2,840.0	10,239.1	3,785.6	2.7047	0.6459
6		90.15	1.8479	14,394.1	0.32	3,145.1	11,248.7	4,165.2	2.7006	0.6449
7		91.94	1.6378	12,741.0	0.26	2,790.8	9,949.9	3,691.6	2.6952	0.6436
8		100.89	1.7964	13,973.2	0.31	3,082.6	10,890.3	4,049.1	2.6896	0.6423
9		102.70	1.7863	13,906.7	0.36	3,069.2	10,837.5	4,026.3	2.6917	0.6428
10		111.28	1.5712	12,229.6	0.41	2,718.6	9,511.0	3,541.5	2.6856	0.6413
11	2098; 0.656	72.133	1.6699	12,687.0	0.29	2,802.1	9,884.6	3,503.5	2.8215	0.6738
12		73.845	1.6582	12,619.8	0.29	2,785.8	9,833.7	3,478.9	2.8267	0.6741
13		80.63	1.8470	14,018.8	0.49	3,119.6	10,898.7	3,875.0	2.8126	0.6716
14		82.40	1.6348	12,395.4	0.48	2,766.1	9,628.8	3,429.8	2.8074	0.6704
15		89.74	1.6865	12,797.8	0.67	2,868.7	9,928.4	3,538.3	2.8060	0.6701
16		100.079	1.8531	14,055.2	1.05	3,178.1	10,876.0	3,887.8	2.7975	0.6680
17		101.989	1.8811	14,238.4	1.05	3,229.8	11,007.5	3,946.5	2.7892	0.6661
18		115.957	1.9538	14,740.2	1.80	3,391.8	11,346.6	4,099.1	2.7681	0.6610
19		117.867	1.8256	13,841.7	1.70	3,174.7	10,665.3	3,830.1	2.7846	0.6650
20	2037; 0.641	64.025	1.8034	13,486.6	1.10	3,006.3	10,479.2	3,673.5	2.8525	0.6812
21		71.71	1.5446	11,541.2	0.49	2,590.3	8,950.4	3,146.4	2.8446	0.6793
22		73.77	2.5121	18,806.0	0.61	4,220.3	14,585.1	5,117.1	2.8503	0.6807
23		85.65	2.1293	15,942.8	0.96	3,609.2	12,332.7	4,337.4	2.8433	0.6790
24		95.16	1.6313	12,192.1	0.95	2,786.3	9,404.8	3,323.0	2.8302	0.6759
25		96.82	1.6235	12,144.9	0.95	2,777.8	9,366.1	3,307.1	2.8321	0.6763
26		106.94	1.7816	13,306.7	1.54	3,071.5	10,234.7	3,629.1	2.8202	0.6735
27		108.529	1.3295	10,025.9	1.30	2,296.0	7,728.6	2,708.2	2.8538	0.6815
28		110.11	1.8020	13,489.1	1.88	3,113.9	10,373.3	3,670.7	2.8260	0.6748
29		115.027	1.7922	13,337.4	2.71	3,109.5	10,225.2	3,650.7	2.8009	0.6689
30	1878; 0.603	71.027	2.3690	16,987.6	1.09	3,972.8	13,013.7	4,449.0	2.9251	0.6985
31		73.37	2.2406	16,061.5	1.09	3,762.0	12,298.4	4,207.8	2.9228	0.6980
32		85.836	1.8709	13,380.9	1.59	3,173.0	10,206.3	3,513.5	2.9049	0.6937
33		100.09	1.7233	12,357.1	2.49	2,955.5	9,399.1	3,236.4	2.9042	0.6935
34		114.335	1.7681	12,648.7	4.05	3,065.9	9,578.7	3,320.5	2.8847	0.6889
35		116.069	1.6369	11,778.9	3.69	2,843.3	8,931.9	3,074.1	2.9055	0.6938
36	1938; 0.553	48.458	1.8239	13,852.3	0.24	3,004.0	10,848.2	3,534.7	3.0690	0.7329
37		52.477	2.0299	15,442.3	0.24	3,351.4	12,090.7	3,933.9	3.0735	0.7340
38		54.317	1.5722	11,967.6	0.24	2,600.4	9,367.0	3,046.9	3.0743	0.7341
39		41.437	1.6416	12,469.9	0.06	2,687.3	9,782.5	3,181.4	3.0749	0.7343
40		43.083	1.6318	12,403.0	0.06	2,674.5	9,728.4	3,162.4	3.0763	0.7346
41		66.539	1.5685	11,941.4	0.60	2,619.4	9,321.4	3,039.8	3.0664	0.7323
42		82.648	1.7483	13,304.3	1.28	2,958.1	10,344.9	3,388.2	3.0532	0.7291
43		84.38	1.6370	12,431.7	1.28	2,773.1	9,657.3	3,172.5	3.0441	0.7269
44		99.906	1.8371	13,963.2	2.06	3,148.8	10,812.3	3,560.3	3.0369	0.7252
45		117.95	1.6837	12,792.5	4.17	2,926.3	9,862.1	3,263.0	3.0224	0.7217
46		119.565	1.4610	11,146.7	3.60	2,543.6	8,599.5	2,831.4	3.0371	0.7253
47	1953; 0.502	29.748	1.6058	12,738.8	0.04	2,603.0	10,135.0	3,136.1	3.2317	0.7717
48		35.54	1.6826	13,349.1	0.05	2,739.3	10,609.7	3,286.1	3.2286	0.7710
49		50.457	1.4594	11,554.7	0.26	2,406.6	9,147.8	2,850.2	3.2095	0.7664
50		52.006	1.5424	12,222.3	0.28	2,546.5	9,675.5	3,012.3	3.2120	0.7670
51		72.099	1.8096	14,343.4	0.67	3,036.5	11,306.2	3,534.1	3.1992	0.7640
52		92.769	1.9901	15,788.6	1.75	3,393.1	12,393.7	3,886.7	3.1887	0.7615
53		112.337	1.7218	13,695.3	2.71	2,982.2	10,710.4	3,362.7	3.1850	0.7606
54		104.13	1.7428	13,864.8	2.23	2,997.7	10,864.9	3,403.7	3.1921	0.7623
55		122.76	1.5013	11,977.5	2.82	2,619.8	9,354.9	2,932.0	3.1906	0.7619
58	2187; 0.759	113.21	1.8830	14,028.2	0.95	3,263.0	10,764.2	4,118.1	2.6139	0.6242
59		123.825	1.9527	14,544.6	1.16	3,411.4	11,132.0	4,270.6	2.6067	0.6225
60	1709; 0.517	27.539	3.8874	27,253.0	0.35	6,328.7	20,923.9	6,643.6	3.1495	0.7521
61		33.29	7.6132	53,382.9	0.70	12,462.8	40,919.4	13,011.0	3.1450	0.7510
62		75.39	5.2698	37,029.1	0.58	8,848.0	28,180.5	9,006.1	3.1290	0.7472
63	1868; 0.517	76.1246	1.2454	9,454.4	0.79	2,113.4	7,340.2	2,326.4	3.1551	0.7534
64		55.238	1.3191	9,991.7	0.35	2,200.3	7,791.0	2,464.1	3.1618	0.7550
65		36.14	1.2249	9,311.0	0.07	2,008.8	7,302.1	2,288.1	3.1913	0.7621

The change in the heat capacity of the calorimeter due to replacing the heating coil by the dilution cup was calculated from the changes in weights of the various materials. The heat capacity of the calorimeter and dilution cup was thus calculated to be 1724 joules per ° C. at 25° C. and 1887 joules per ° C. at 100° C. A linear relation between the heat capacity and temperature was assumed.

Specific Heats

Eight to ten determinations of specific heat were made on each solution at different temperatures between 30° and 122° C. (86° and 252° F.). All measurements were made above the crystallizing temperature of the solution.

In preparation for a series of measurements, sufficient sodium hydroxide solution of known composition was weighed into the bomb to bring the level to within about 2 cm. (3/4 inch) of the top. The added displacement of the heater and thermal sheaths displaced brought the level to within 1 cm. (3/8 inch) of the top. In the specific heat determinations the total liquid volume was approximately 1400 cc.

The submarine jacket was bolted in place and the entire assembly immersed in the bath equipped for electrolytic heating. The bomb and solution were brought to the desired temperature by passing current through the quantitative heating coil, and an auxiliary heating coil was installed for this purpose. The temperature of the surrounding bath was also brought to the same level by use of electrolytic conduction heating and an auxiliary steam coil.

After the desired temperature was reached, the current was cut off from the electric heaters in the bomb and the magnetic stirring smoothed out inequalities of temperature between the solution and the bomb. Sufficient heat was generated in the surrounding bath to maintain an adiabatic condition, and readings were taken to determine the change of the solution

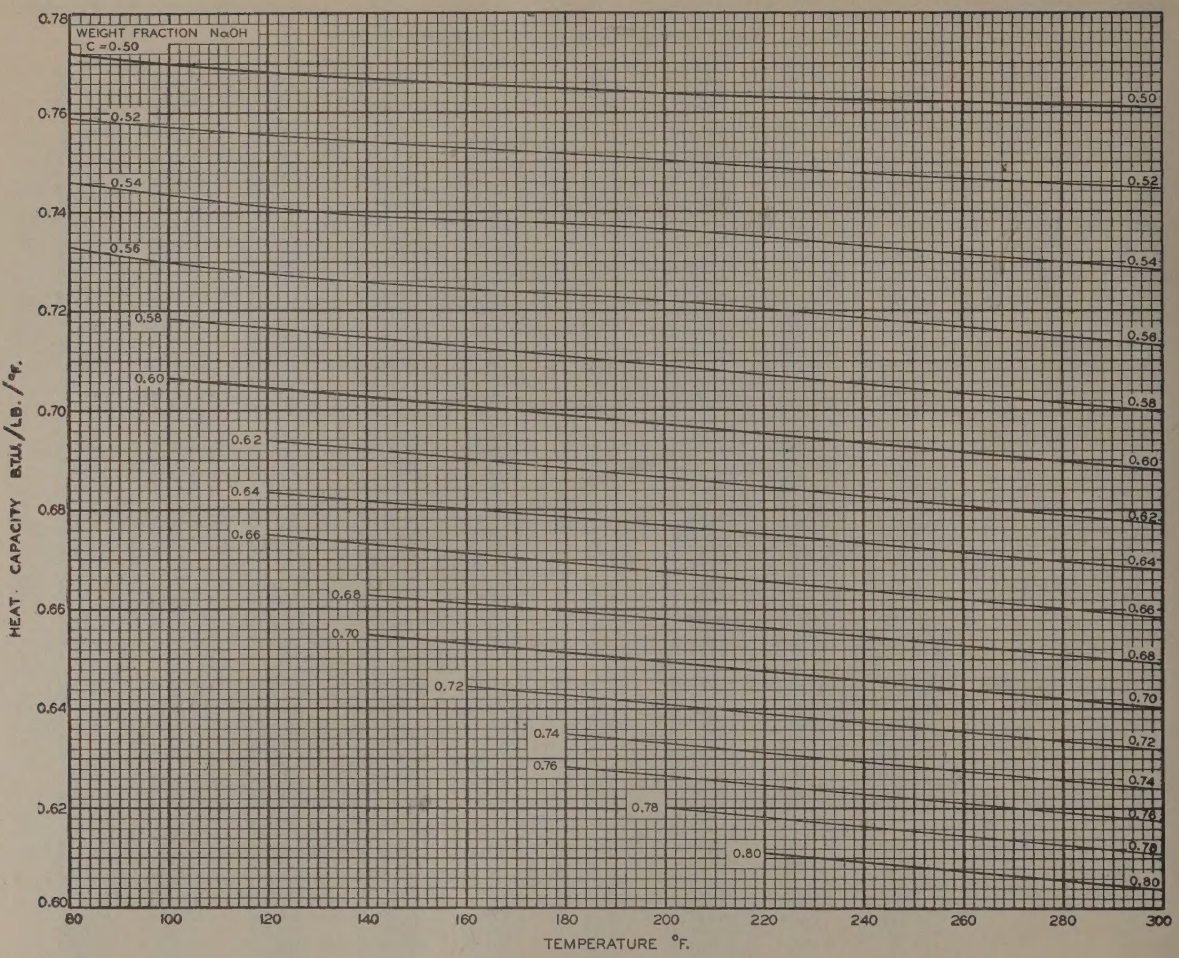

Figure 8.—Specific Heats *vs.* Temperatures at Even Concentrations

temperature with time. A period of 20 to 30 minutes was usually sufficient to establish a linear drift.

By means of a precision timing device the current was then connected to the quantitative heating coil for an accurately measured heating period during which additional heat was supplied to the surrounding bath to maintain adiabatic conditions. The method of arriving at the rise in temperature due to the electrical heat input was outlined above.

The results of sixty-five specific heat measurements are given in Table I. These results were plotted as lines of constant composition on coordinates of specific heat and temperature, and smooth curves were drawn through the points. Values for the given solutions at even temperature intervals were read from the curves. The values at even temperatures were then plotted on coordinates of specific heat and concentration as lines of constant temperature. From these curves values of specific heat at even temperatures and even concentrations were obtained (Table II). These values were then cross-plotted to form the curves of Figure 8, showing the specific heats at even values of concentration as a function of temperature.

Above a concentration of 56 per cent sodium hydroxide the specific heats were found to be linear with respect to temperature over the range of temperatures covered by the data.

Heats of Dilution

The general procedure was outlined in a previous section. Integral heats of dilution were measured at various mean temperatures above or below 200° F. but were corrected to that temperature by means of previously determined specific heats in the same range of concentration and temperature. The method of integral stepwise dilutions was used. A solution of maximum concentration was diluted with a solution of lower concentration; a product of intermediate concentration was obtained which was then used as the concentrated solution, and the process was repeated until a concentration well within the range covered by Bertetti and McCabe (*1*) resulted.

In this work it was not necessary to carry the stepwise dilutions to a very low value approaching infinite dilution because values of enthalpy for sodium hydroxide solutions up to 50 per cent NaOH content and at temperatures up to 210° F. were available from the work of Bertetti and McCabe (*1*). Thus dilutions were carried out starting with a concentration of 75.5 per cent and finishing with one of 46.4 per cent sodium hydroxide.

A 46 per cent solution was used in the dilution cup for the first two dilutions to avoid the rapid rise in temperature that might result if water were employed; the concentrated solu-

Table II. Specific Heats of Sodium Hydroxide Solutions

Concn., Wt. % NaOH	B. t. u. per Pound per ° F.											
	80° F.	100° F.	120° F.	140° F.	160° F.	180° F.	200° F.	220° F.	240° F.	260° F.	280° F.	300° F.
50	0.772	0.770	0.768	0.767	0.766	0.765	0.764	0.763	0.762	0.762	0.761	0.761
52	0.759	0.757	0.756	0.754	0.753	0.752	0.751	0.749	0.748	0.747	0.746	0.745
54	0.746	0.744	0.741	0.739	0.739	0.738	0.737	0.735	0.733	0.731	0.730	0.728
56	0.733	0.730	0.728	0.726	0.724	0.723	0.722	0.721	0.719	0.717	0.715	0.713
58	...	0.719	0.717	0.715	0.713	0.711	0.709	0.707	0.705	0.703	0.702	0.700
60	...	0.706	0.705	0.703	0.701	0.699	0.697	0.695	0.693	0.691	0.690	0.688
62	...	...	0.694	0.692	0.690	0.688	0.687	0.685	0.683	0.681	0.679	0.677
64	...	...	0.684	0.682	0.681	0.679	0.677	0.675	0.673	0.671	0.670	0.668
66	...	...	0.675	0.673	0.671	0.669	0.668	0.666	0.664	0.662	0.660	0.658
68	...	...	...	0.663	0.662	0.660	0.658	0.656	0.655	0.653	0.651	0.649
70	...	...	...	0.655	0.653	0.651	0.649	0.647	0.646	0.644	0.642	0.640
72	...	...	...	...	0.645	0.643	0.641	0.639	0.637	0.635	0.634	0.632
74	...	...	...	...	...	0.635	0.633	0.631	0.629	0.628	0.626	0.624
76	...	...	...	...	...	0.628	0.627	0.625	0.623	0.621	0.619	0.617
78	...	...	...	...	...	...	0.620	0.618	0.616	0.615	0.613	0.611

tion was in the bomb. No difficulty was experienced in controlling the mixing of the 46 per cent with the more concentrated solution. A 19.74 per cent solution was used for dilution steps from 73 to 60 per cent. For dilutions below 60 per cent, distilled water was the diluting liquid until the final concentration of 46.4 per cent was reached.

In preparing for a heat of dilution measurement, dilute solution or distilled water was weighed at room temperature in the dilution cup. The cup was screwed into place against the packing, and sufficient thickness of gasket was used to provide a vapor-tight seal when the cup was in the required position for coupling the valve stems.

The concentrated solution was heated in the bomb to 90–95° C. (194–203° F.) and weighed just before assembly. Corrections were applied for convection currents, unequal length of balance arms, and buoyancy of air. After assembly in the calorimeter the temperature of the bomb and contents were adjusted further by immersing the bomb temporarily in a water bath while the solutions were agitated by the magnetic stirrers.

The water bath was removed, the submarine jacket was bolted in place, and the bath for electrolytic heating, preheated to 90–95° C. with a steam coil, was elevated to immerse the submarine. The bath stirrers were started, and the electrolytic heating current was adjusted to maintain an adiabatic condition just as in the specific heat determinations. A foreperiod of constant drift of temperature with time was established before starting the dilution by "cracking" one of the mixing valves. When the valves were opened wide, a temporary deviation from adiabatic condition took place. These were compensated by carrying the bath temperature higher than the bomb by about the same difference with heat flowing in the reverse direction for about the same length of time. If necessary the rate of mixing was reduced by temporarily stopping the stirrers. After several minutes of careful dilution the valve was fully opened, and after about 10 minutes mixing was complete. An afterdrift period was established and the temperature rise for the experiment was obtained from these time-temperature drift plots as in the specific heat determinations. The observations were the same as those taken in a specific heat determination, except for measurements of time, voltage, and amperage, which were not necessary.

The heat effect of a dilution was calculated from the measured temperature rise of the calorimeter and its contents, from the known heat capacity of the calorimeter, and from the known specific heat of the final solutions. The usual vaporization correction was applied.

Thermodynamically the heat effect, Q, is

$$Q = w_2h_2 - w_1h_1 - w_dh_d \qquad (2)$$

where Q = heat absorbed by dilution (negative in these experiments)

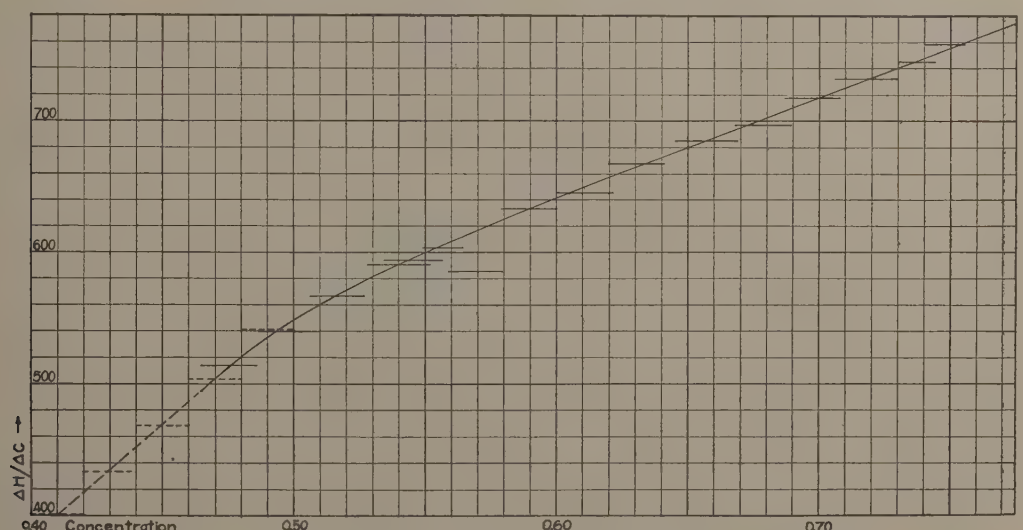

Figure 9. Heats of Dilution at 200° F.

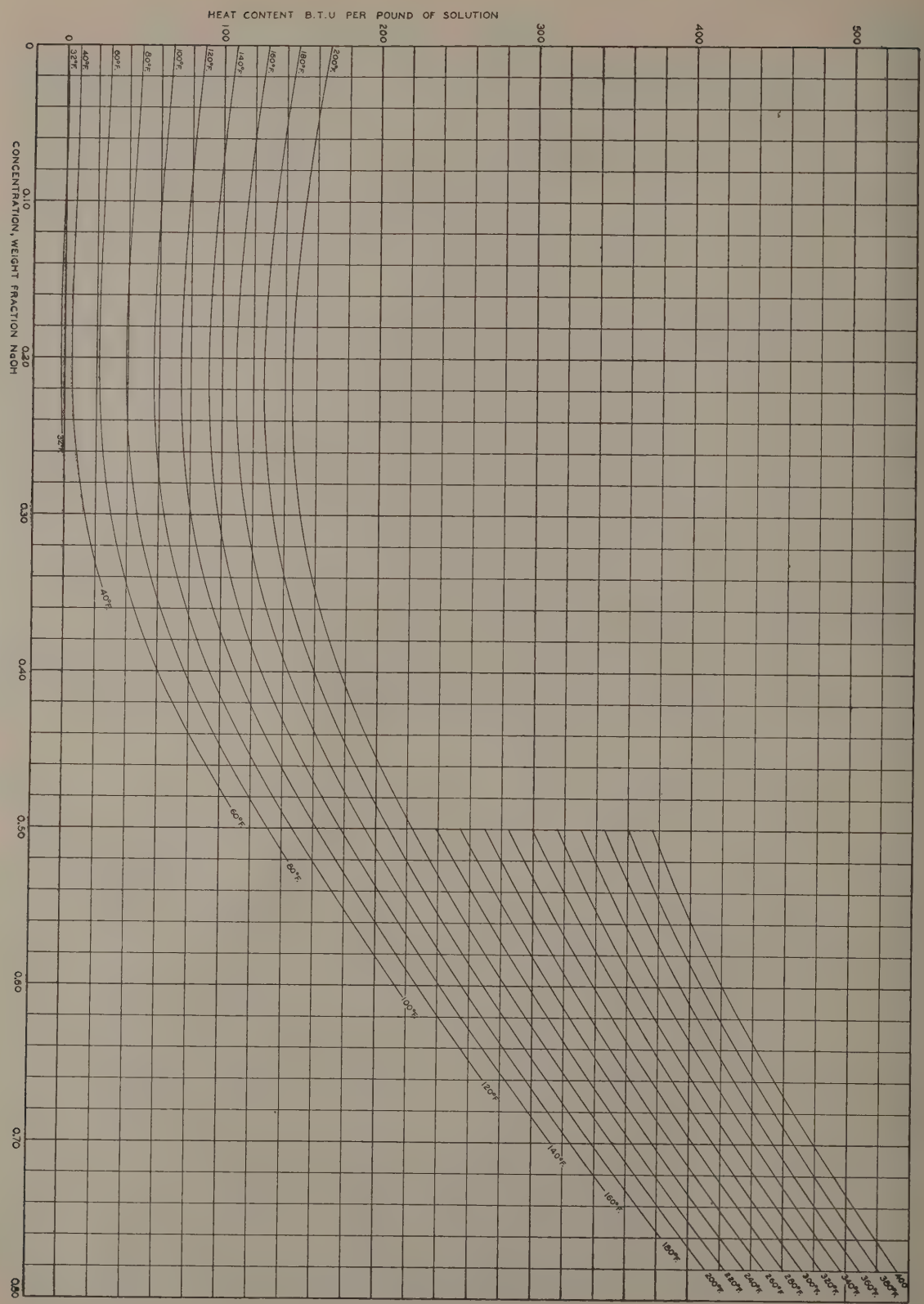

Figure 10. Enthalpy-Concentration Chart

TABLE III. RESULTS OF HEAT OF DILUTION DETERMINATIONS

Concn., Wt. Fraction NaOH Initial, C_a	Final, C_b	Heat Content, B. T. U./Lb. Initial, h_a	Final, h_b	$\frac{\Delta h}{\Delta C}$
0.7551	0.7404	391.44	380.3	758
0.7442	0.7301	383.00	372.5	745
0.7304	0.7068	373.27	356.0	731.7
0.7076	0.6869	356.31	341.45	717.8
0.6888	0.6677	342.71	328.00	697.1
0.6681	0.6453	328.27	312.65	685.0
0.6419	0.6204	310.35	296.00	667.4
0.6219	0.6006	297.00	283.25	645.5
0.6003	0.5783	283.18	269.25	633.1
0.5785	0.5558	269.04	255.75	585.4
0.5568	0.5343	256.47	243.1	594.2
0.5687	0.5485	263.7	251.5	603.9
0.5517	0.5278	253.23	239.11	590.1
0.5269	0.5065	238.60	227.04	567
0.5090	0.4868	228.38	216.39	540
0.4864	0.4643	216.17	204.8	514

w_1 = mass of concentrated solution
w_2 = mass of final solution after dilution
w_d = mass of diluting solution
h_1 = specific enthalpy of concentrated solution before dilution
h_2 = specific enthalpy of final solution after dilution
h_d = specific enthalpy of diluting solution

Equation 2 is applied first to the data from the final dilution of the series. In this case all terms except h_2 are known or measured, and h_2 can be calculated. Since the product of one experiment is the concentrated solution charged to the next experiment, Equation 2 is applied successively to the data from the next to the last dilution, and the procedure is continued until the specific enthalpy of the most concentrated solution used in the first dilution is determined. If it is desired to correct any enthalpy to an arbitrary temperature, the correction is made by means of specific heats in the usual way.

The heats of dilution were calculated and corrected to 200° F. The final results are shown as specific enthalpies in Table III. The table also shows values of $(h_2-h_1)/(C_2-C_1)$ or $\Delta h/\Delta C$. The values of $\Delta h/\Delta C$ are plotted as line segments *vs.* C in Figure 9. The dotted segments show the results of Bertetti and McCabe (*1*) for concentrations below 50 per cent. The line in Figure 9 was drawn to smooth the stepwise enthalpy values and give a "base isotherm" of an enthalpy-concentration chart.

Enthalpy-Concentration Chart

From the data of Bertetti and McCabe and those of the present work an enthalpy-concentration chart (Figure 10) for solutions of sodium hydroxide and water over a concentration range of 0 to 78 weight per cent sodium hydroxide and a temperature range of 32° to 400° F. was prepared (*3*). Specific enthalpies over the concentration range 50 to 78 per cent are listed in Table IV. The enthalpies in the range 250° to 400° F. are based on extrapolated specific heats and are therefore less accurate than those at lower temperatures. They should be accurate enough for engineering purposes.

Acknowledgment

The following companies contributed to the support of this work: Buffalo Foundry and Machine Company, The Mathieson Alkali Works (Inc.), Michigan Alkali Company, Pennsylvania Salt Manufacturing Company, Pittsburgh Plate Glass Company, Solvay Process Company, Swenson Evaporator Company. The work was carried out as a project of the Department of Engineering Research, University of Michigan.

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ABSTRACTED from a dissertation submitted by H. R. Wilson in partial fulfillment of the requirements for the degree of doctor of philosophy, University of Michigan.

TABLE IV. HEAT CONTENT OF SODIUM HYDROXIDE SOLUTIONS

(Standard states: H_2O, liquid at 32° F.; NaOH, infinitely dilute solution at 68° F.)

Temp., ° F.	Heat Content, B. T. U. per Pound of Solution at Concentration of: 50%	52%	54%	56%	58%	60%	62%	64%	66%	68%	70%	72%	74%	76%	78%
80	131.33	114.11	157.43	171.06	....	....	....	....	....	....	....	....	....	....	....
90	139.05	151.70	164.88	178.39	....	....	....	....	....	....	....	....	....	....	....
100	146.76	159.27	172.33	185.69	199.20	213.08	....	....	....	....	....	....	....	....	....
110	154.46	166.84	179.76	192.99	206.38	220.14	....	....	....	....	....	....	....	....	....
120	162.15	174.40	187.17	200.27	213.55	227.19	241.01	255.09	269.42	....	....	....	....	....	....
130	169.83	181.95	194.58	207.54	220.71	234.23	247.95	261.93	276.15	....	....	....	....	....	....
140	177.50	189.50	201.97	214.80	227.87	241.27	254.88	268.75	282.90	297.38	312.08	....	....	....	....
150	185.17	197.03	209.36	222.06	235.01	248.29	261.79	275.57	289.63	304.00	318.62	....	....	....	....
160	192.83	204.56	216.75	229.30	242.14	255.30	268.70	282.38	296.34	310.62	325.16	339.99	....	....	....
170	200.48	212.09	224.13	236.55	249.26	262.30	275.60	289.18	303.05	317.22	331.68	346.43	....	....	....
180	208.13	219.61	231.51	243.78	256.38	269.30	282.49	295.97	309.75	323.83	338.20	352.86	367.72	383.05	....
190	215.78	227.12	238.88	251.01	263.48	276.28	289.37	302.76	316.44	330.42	344.70	359.29	374.16	389.33	....
200	223.42	234.63	246.25	258.24	270.58	283.26	296.24	309.53	323.12	337.01	351.20	365.70	380.50	395.60	411.01
210	231.06	242.13	253.61	265.46	277.67	290.23	303.10	316.30	329.79	343.59	357.69	372.10	386.82	401.86	417.20
220	238.69	249.63	260.97	272.67	284.74	297.17	309.95	323.05	336.45	350.16	364.17	378.50	393.14	408.11	423.39
230	246.32	257.11	268.31	279.87	291.81	304.11	316.80	329.80	343.10	356.72	370.63	384.88	399.45	414.35	429.57
240	253.94	264.59	275.65	287.06	298.87	311.05	323.63	336.54	349.75	363.27	377.10	391.26	405.85	420.59	435.74
250	261.57	272.06	282.97	294.24	305.94	317.98	330.45	343.26	356.38	369.81	383.54	397.62	412.23	426.81	441.89
260	269.19	279.53	290.29	301.41	312.98	324.90	337.26	349.99	363.00	376.34	389.99	403.98	418.51	433.02	448.04
270	276.81	287.00	297.60	308.58	320.01	331.81	344.06	356.70	369.62	382.86	396.42	410.33	424.78	439.23	454.18
280	284.42	294.42	304.91	315.73	327.03	338.71	350.96	363.40	376.22	389.37	402.84	416.67	431.04	445.43	460.32
290	292.04	301.91	312.20	322.88	334.04	345.60	357.84	370.09	382.82	395.88	409.26	423.00	437.30	451.61	466.44
300	299.65	309.35	319.49	330.01	341.04	352.48	364.62	376.77	389.41	402.37	415.66	429.32	443.54	457.79	472.55
310	307.26	316.79	326.77	337.15	348.09	359.36	371.40	383.45	396.00	408.86	422.07	435.64	449.78	463.97	478.66
320	314.87	324.23	334.05	344.28	355.03	366.23	378.17	390.12	402.58	415.34	428.47	441.95	456.01	470.14	484.75
330	322.48	331.66	341.32	351.39	362.02	373.10	384.93	396.78	409.15	421.82	434.86	448.25	462.23	476.30	490.86
340	330.08	339.09	348.59	358.49	369.00	379.96	391.68	403.43	415.71	428.29	441.24	454.54	468.44	482.45	496.95
350	337.68	346.51	355.84	365.58	375.97	386.81	398.42	410.08	422.26	434.75	447.61	460.82	474.64	488.59	503.03
360	345.27	353.93	363.08	372.67	382.93	393.65	405.15	416.72	428.80	441.20	453.97	467.09	480.84	494.72	509.10
370	352.86	361.34	370.31	379.75	389.88	400.48	411.87	423.35	435.33	447.64	460.32	473.36	487.03	500.84	515.16
380	360.45	368.75	377.53	386.82	396.82	407.30	418.58	429.97	441.85	454.07	466.66	479.62	493.21	506.95	521.21
390	368.04	376.16	384.74	393.88	403.75	414.11	425.28	436.58	448.36	460.49	472.99	485.87	499.38	513.05	527.25
400	375.62	383.57	391.95	400.93	410.67	420.91	431.97	443.18	454.87	466.49	479.31	492.11	505.54	519.14	533.28

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